Effect of Wax Addition on Gel-to-Liquid-Crystalline Phase Transition of Palm-Oil as Studied by FT-IR Spectroscopy (Commemoration Issue Dedicated to Professor Tohru Takenaka On the Occasion of His Retirement)

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NOTE

Effect of Wax Addition on Gel - to - Liquid-Crystalline Phase Transition of Palm-Oil as Studied by FT-IR Spectroscopy

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Effect of wax addition on gel - to - liquid-crystalline phase transition of palm-oil was studied by FT-IR sectroscopy. In the presence of 0.4% wax, low-frequency shift of the antisymmetric and symmetric CH_2 stretching bands was observed at all the temperatures examined. In contrast, same amount of wax did not affect the polar group bands. These results suggest that wax interacts with the hydrophobic part of the palm-oil molecules selectively. Plausible mechanism of the interaction between wax and the CH chain of palm-oil is also proposed.

KEY WORDS: Palm-oil / Carnauba wax / Gel-to - liquid-crystalline phase transition / FT-IR spectroscopy

Introduction

The stability of oil/water emulsion is one of the most crucial subjects for food industries. It is considered that the structure, conformation, and the order of oil molecules are closely related to the emulsion stability. So far, however, there is few consideration about the molecular mechanism determining the emulsion stability.

Recently it is found that carnauba wax comprising alcohol fatty-acid ester (30% of which containing hydroxy acid) has noticeable stabilizing effect on palm-oil emulsion. From differential scanning calorimetric (DSC) studies, it is also demonstrated that wax affects the thermal phase behavior of palm-oil itself; the DSC curve becomes sharper and shows increased cooperativity in the precence of wax (unpublished data). Although this implies highly-ordered state or increased crystallinity of palm-oil molecules, the molecular mechanism of the effect of wax addition is not fully understood.

Fourier-transform infrared (FT-IR) spectroscopy is a powerful tool to analyze structure and orientation of each functional group of molecules independently. We therefore apply FT-IR tramsmission spectroscopy to the system of palm-oil in the presence and the absence of wax. Special attention is focused on the effect of wax on gel - to -liquid-crystalline phase transition of palm-oil, from which we find different mechanism of interaction between wax and each functional group of the palm-oil molecules.

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Experimental

Materials. Palm-oil, mainly consisting of triglyceride, and carnauba wax were provided by Fuji Oil Company, Ltd. Dominant fatty-acid components of palm-oil, determined by gas chromatgraphy, were 40.8% lauric acid, 24.1% oleic acid, 12.0% myristic acid, and 7.6% palmitic acid. The melting point was 20.4℃. Wax contained saturated long-chain fatty acids with carbon numbers from 16 to 33; mainly 27.4% of C_{24} acid and 14.1% of C_{28} acid. The melting point of wax was 83.5℃.

Sample preparation. Palm-oil or the mixture of oil + 0.4% wax was sandwiched with CaF_2 cells. The sample thickness was estimated about several microns. Each sample was then annealed for at least 1h at 26℃ (above the phase transition temperature) to obtain homogeneous state. In order to regulate the temperature, the cell was placed in a Harrick-type hollow cell mount thermostatically controlled by a Neslab model RTE-4 refrigerated-bath circulator using a 1:1 mixture of ethylene glycol and water. The temperature of the sample was monitored by a copper-constantan thermocouple inserted into the cell. The accuracy of the temperature control and reading was within ±0.1℃.

FT-IR measurement. FT-IR transmission spectra in the temperature range from 15 to 23℃ were recorded on a Nicolet 710 FT-IR spectrophotometer equipped with a mercury cadmium telluride detector. Each spectrum was measured after the sample was heated to a predetermined temperature and left for 5 min to reach thermal equilibrium. One hundred interferograms, collected with the maximum optical retardation of 0.25 cm, were accumulated to yield spectra of high S/N ratio with resolution of 4 cm^{-1}. The accuracy of the frequency reading was better than ±0.1 cm^{-1}.

Results and Discussion

Spectral change characteristic of the gel - to - liquid-crystalline phase transition of palm-oil.

Before considering the effect of wax addition on the thermal phase behavior of palm-oil, we investigate the spectral features characteristic of the thermal behavior of palm-oil itself.

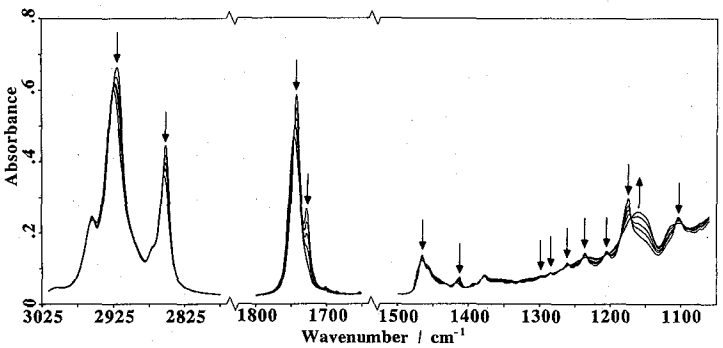

Fig.1 FT-IR transmission spectra of palm-oil measured at 15, 19, 20, 22, and 23℃. Arrows indicate the direction of the spectral change of each band on the heating process.

Figure 1 demonstrates FT-IR transmission spectra of palm-oil on heating from 15 to 23℃. Assignments of the major absorption bands are summarized in Table I in the case of gel phase, according to the previous IR studies of tripalmitin[1] and phospholipids.[2-5]

Table I Assignments of the major absorption bands of palm-oil in the gel phase

Wavenumber/cm^{-1}	Assignment
2955	Asymmetric CH_3 stretching
2920	Antisymmetric CH_2 stretching
2851	Symmetric CH_2 stretching
1742,1727	Ester C=O double bond stretching
1466	CH_2 scissoring
1413	α -CH_2 scissoring
1378	Symmetric CH_3 bending
1300-1200	CH_2 wagging band progression with CH_2 groups in all-*trans* configuration
1175,1160	Ester CO-O single bond sretching
1104	Glycerol C-C stretching

In Fig.1, several temperature-dependent spectral changes are noticed. With regard to the CH bands, the antisymmetric and symmetric CH_2 stretching bands at 2920 and 2850 cm^{-1} are shifted to the high-frequency side with increasing the temperature, which is characteristic of gel - to - liquid-crystalline phase transition.[6] Besides the regularly-spaced bands in the region 1300-1200 cm^{-1}, which are ascribed to the CH_2 wagging band progression resulting from the wagging vibrations of all-*trans* conformers, disappear above the gel - to - liquid-crystalline phase transition temperature (Tc = 20.4℃), indicating that the proprotion of *gauche* conformers in the CH chains is increased at Tc.[7]

Temperature-dependent spectral changes are also found for polar head group bands. First, The ester C=O stretching bands at 1750-1720 cm^{-1} are clearly split into two components. The high-frequency component is observed at 1742 cm^{-1} in the gel phase, but broadened and shifted to higher frequency upon heating. In constrast, the low-frequency component at 1727 cm^{-1} almost unaltered its position. However, this band is gradually weakened with increasing the temperature, and finally disappears above Tc. The two components of the C=O stretching band are not definitely assigned. But it is reasonable to consider that they are due to the C=O group of different conformation; low-frequency component corresponds to the conformers with limited freedom ('bound' conformers) and high-frequency component to those with relatively high freedom ('free' conformers). Upon heating the number of 'bound' conformers is decreased because of the increase in the librational motion, which induces the disappearance of the low-frequency component. Simultaneously, the high-frequency component is shifted to the higher position and broadened, as a result of the increased motion of the 'free' conformers.

Another temperature-dependent spectral change is noticed for the ester CO-O single bond

stretching bands at 1180–1150 cm^{-1}. There are also two components in this band; the high-frequency component at 1175 cm^{-1} is diminished with increasing the temperature, while low-frequency component around 1160 cm^{-1} is gradually increased. The result suggests temperature-induced conformational changes including a change of dihedral angles around the CO–O bonds in the ester part of the molecules.[1)]

Effect of wax addition on the thermal behavior of palm-oil.

In order to identify the effect of wax on the gel - to - liquid-crystalline phase transition of palm-oil, temperature dependence of the FT-IR transmission spectra is also measured in the case of palm-oil containing 0.4% of carnauba wax. Although CH chains are also included in wax, they are not substantially contributed to the measured spectra because of the small content of wax, as compared to that of palm-oil.

There are different effects of wax addition on the temperature-dependent change of CH bands and that of polar group bands. In antisymmetric and symmetric CH_2 stretching bands, the shift to the low-frequency side is observed at all the temperatures examined, as demonstrated in Fig.2a for the symmetric CH_2 stretching band. The low-frequency shift of both CH_2

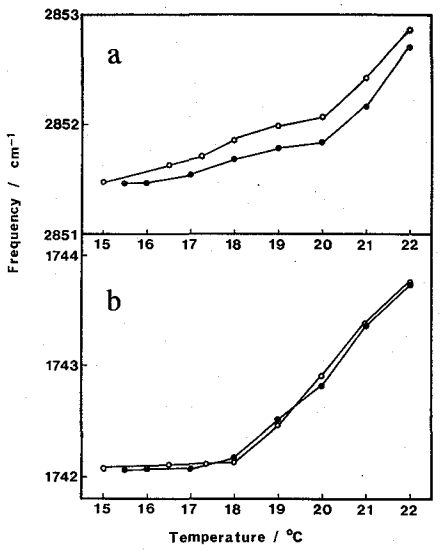

Fig.2 Temperature dependence of the frequencies of (a) the symmetric CH_2 stretching band and (b) the ester C=O stretching band in the IR spectra of palm-oil containing 0.4% wax (●) and without containing wax (○).

stretching bands indicates that the CH chains are solidified (crystallized) and well-oriented with the increase in the number of all-*trans* conformers.[5)] Therefore this result implies that the CH chains of the palm-oil molecules are solidified and well-ordered by the wax addition. The present result is consistent with that deduced from the DSC curves in the same system

with increased sharpness and cooperativity mentioned before. In addition, the result that the surface-pressure - area isotherm of a palm-oil monolayer containing wax exhibits more condensed state of the CH chains of palm-oil in comparison with that of a pure palm-oil in monolayer (unpublished data) also confirms our spectroscopic result.

Figure 2b shows the temperature-dependent frequency change of the C=O stretching band of palm-oil in the presence and the absence of wax. No appreciable effect of wax is found, which is a remarkable contrast to the low-frequency shift of the CH_2 stretching band shown in Fig.2a. The absence of wax effect is also noticed for the ester CO-O single bond stretching band and glycerol C-C stretching band (not shown).

From these results it is concluded that the wax interacts the hydrophobic part of palm-oil and crystallizes the CH chains selectively. A series of saturated long CH chains (C_{16}-C_{33}) of wax are contributed to this hydrophobic interaction and solidified the CH chains of palm-oil. Moreover, it is reasonable to consider that the mechanism of crystallization and reorientation of the CH chains of palm-oil induced by the wax addition is also related to the palm-oil emulsion-stabilizing effect.

Finally it should be noted that the present method of FT-IR spectroscopy provides strong evidence of the molecular mechanism of the emulsion-stabilizing process, which is useful in many industrial fields.

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